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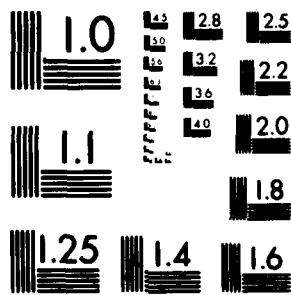
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Using resonant Raman scattering at the $E_g$ gap we have investigated the scattering by coupled LO phonon-collective inter-subband charge carrier excitation in quasi-two-dimensional plasmas at the InAs surface of MOS junctions found on n- and p- InAs surfaces. Our investigation of giant Raman scattering by adsorbed molecules on a rough Ag surface has shown a major contribution comes from the enhancement		

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20. ABSTRACT CONTINUED

of the incident and scattered EM fields that results from the excitation of the collective electron resonance of microstructures, eg bumps, on the surface.

Evidence is presented, on the basis of a study of the resonance Raman scattering by crystal violet molecules adsorbed on smooth Ag and Au surfaces, for a sizeable contribution to the surface enhanced Raman scattering that depends on the specific nature of the chemisorption of the molecules by the metal surface.

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RAMAN SPECTROSCOPY OF SOLIDS

FINAL REPORT

ELIAS BURSTEIN

DECEMBER 28, 1981

U.S. ARMY RESEARCH OFFICE

CONTRACT NUMBER DAAG29 80 C 0066

UNIVERSITY OF PENNSYLVANIA

PHILADELPHIA, PENNSYLVANIA 19104

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## I. STATEMENT OF THE KEY PROBLEMS STUDIED

The investigation of the inelastic scattering of light by the elementary excitations of a medium is a powerful technique for obtaining information about the mode parameters and symmetries of the excitations, the relevant microscopic processes, and the electronic structure of the medium. Our own experimental and theoretical research supported by ARO during the period 1 October 1979 to 31 October 1981 has been concerned with the following major problems:

- 1) Inelastic Scattering of Light by Charge Carrier Excitations in Quasi-Two-Dimensional Plasmas.
- 2) Giant Raman Scattering by Molecules Adsorbed on Metal Surfaces.
- 3) Raman Scattering by Resonant Molecules at Smooth Ag and Au Surfaces.

## II. SUMMARY OF THE MOST IMPORTANT RESULTS

### 1. Inelastic Scattering of Light by Charge Carrier Excitations in Quasi-Two-Dimensional Plasmas<sup>1,3</sup>.

On the basis of a theoretical analysis of the microscopic mechanisms for the inelastic scattering of light by charge carrier excitations in semi-conductors, we had earlier proposed that it should be readily feasible, using resonance enhancement at the  $E_0 + \Delta_0$  gap of III-V semiconductors, to observe the inelastic scattering of light by inter-subband charge carrier excitations in quasi-two-dimensional plasmas that occur in accumulation and inversion layers at semiconductor surfaces and to obtain, thereby, information about the single-particle and collective inter-subband excitations. Moreover, we noted<sup>1</sup> that it might also be feasible to observe the inelastic light scattering, by coupled LO phonon-collective inter-subband excitation modes (the analogs of the coupled LO phonon-plasmon modes in bulk semi-conductors), at the  $E_1$  gap.

The inelastic light scattering by non-spin flip and spin-flip inter-subband excitations has since been reported by Abstreiter and Ploog (Phys. Rev. Lett. 42, 1308 (1979)) and by Pinczuk et al (Solid State Communications 32, 1001 (1979)) among others. Inelastic light scattering has in fact, become a powerful tool for the investigation of the charge carrier excitations of two-dimensional plasmas.

On the experimental side we have carried out an investigation of the resonant Raman scattering at the  $E_1$  gap by LO phonons and their coupled modes with plasmons at the InAs surfaces of MOS junctions formed in n- and p- InAs substrates.<sup>3</sup> Our data show that under zero-gate bias conditions, the surfaces of the n-InAs substrates are strongly accumulated and the surfaces of the p-InAs substrates are strongly inverted. Moreover the resonant Raman scattering at the  $E_1$  gap from the InAs surface in MOS junctions of low density

n- and p-InAs substrates exhibit, under zero- and positive-gate bias conditions, a narrow peak at a frequency ( $236\text{ cm}^{-1}$ ) that is intermediate between that of the TO phonons and that of unscreened LO phonons. The width and strength of the peak are comparable to those of the peak due to unscreened LO phonons. Moreover the position of the peak does not change perceptively when the gate voltage is increased from 0 V to + 40 V, ie, when the density of the electrons at the surface is increased. Since this behavior is similar to that expected for LO phonons screened by collective inter-subband excitations, the peak at  $236\text{ cm}^{-1}$  is attributed to inelastic light scattering via the Frohlich three-step scattering mechanism by coupled LO phonon-collective inter-subband charge carrier excitations. These results constitute confirmation of our earlier suggestion that it should be possible to observe resonance Raman scattering by coupled LO phonon-inter-subband charge carrier excitations at the  $E_g$  gap.

## 2. Giant Raman Scattering by Molecules Adsorbed at Metal Surfaces<sup>2,4,5</sup>.

Although it was quite evident that surface roughness on a sub-microscopic scale plays a crucial role in the giant enhancement of the Raman scattering by molecules adsorbed at a Ag electrode, there was no consensus regarding the mechanisms that were involved. We had proposed, in earlier work, that the microscopic mechanisms involved surface roughness enhanced electron-hole pair excitation and recombination. On the basis of the analogy to the enhancements that occur when surface-EM modes are used as the incident and scattered EM radiation, we had also conjectured that the excitation of the collective electron resonances of submicroscopic bumps on the rough metal surface leads to an enhancement of the EM fields at the adsorbed molecules.<sup>2</sup>

To elucidate the role of the collective electron resonances of the rough metal Ag surface, we carried out a detailed experimental investigation



of the Raman scattering by molecules (eg, isonicotinic acid and benzoic acid) adsorbed on Ag island films. The enhancements in the Raman scattering by the molecules adsorbed on the Ag island film were found to be comparable in magnitude to that for pyridine adsorbed on a Ag electrode. We also found that the wavelength dependent intensity of the Raman peaks was approximately proportional to the square of the absorptance of the Ag island film.

To obtain further information about the contribution to the enhanced Raman scattering which arise from the excitation of the collective electron resonances of the Ag island film, we carried out a theoretical analysis of the differential scattering cross-section for molecules adsorbed at an idealized Ag island film consisting of an ordered array of metal ellipsoids (island) on a flat dielectric substrate. The results of this theoretical analysis, reported in Physical Review Letters<sup>4</sup> showed that there were major contributions to the enhancement from the increase in the incident electric field at the adsorbed molecules and the increase in the electric dipole moment of the metal ellipsoid-adsorbed molecule complex that result from the excitation of the transverse collective electron resonance of the Ag island film. Our estimate for the idealized model indicated an overall enhancement of the order of  $10^6$  to  $10^7$ . This estimate is obviously on the high side. In an actual evaporated Ag island film the islands are random in size, shape and orientation, and furthermore are not strictly ellipsoidal. As a consequence the transverse collective electron resonance is inhomogeneously broadened and the contributions to the Raman scattering intensity from the enhancement of the incident and scattered EM fields is appreciably smaller.

There are still unanswered questions regarding the role played by chemisorption of the molecules the metal surface. That chemisorption plays some role is indicated by the marked differences that occur in the Raman scattering by isonicotinic acid and benzoic acid when using Ag island

films as substrates and as overlayers. Thus, the Raman scattering by benzoic acid is only observed when the Ag island film is used as substrate, whereas the Raman scattering by isonicotinic acid is observed when the Ag island film is used either as substrate or as overlayer. It has been, and still is, our contention that the overall enhancement is the result of a combination of contributions - surface roughness enhanced incident and scattered EM field, surface roughness enhanced electron-hole pair excitation and recombination, charge-transfer excitations and other specific electronic structure effects of chemisorption.

### 3. Raman Scattering by Resonant Molecules at Smooth Ag and Au Surfaces.

We have carried out an investigation of the resonance Raman scattering by crystal violet adsorbed from dilute aqueous solutions onto "smooth" evaporated films of Ag and Au. Our objectives in this investigation was to study the Raman scattering by molecules on a "smooth" metal surface, whose Raman scattering cross-section was sufficiently large to be observable without the enhancement of the incident and scattered electromagnetic fields by surface roughness, in order to obtain information about other contributions to the Raman scattering cross-section (e.g. the effect of chemisorption). Crystal violet, a triphenylmethane type dye which exhibits overlapping absorption bands at  $\sim 5500 \text{ \AA}$  and at  $\sim 5890 \text{ \AA}$  and a broad luminescence band at  $\sim 6700 \text{ \AA}$ , satisfied this criterion. The Raman scattering by a monolayer of crystal violet on glass is observable, although dominated by a relatively strong luminescence. We find that the Raman scattering intensity of a monolayer of the molecules on a smooth Ag surface is about the same as that of a monolayer of the molecules on glass. On the other hand the Raman scattering intensity of

a monolayer of molecules on a smooth Au surface is greater by an order of magnitude than that of the monolayer on Ag, even at wavelengths below 5200 Å, the onset of interband transitions where there is little, if any, enhancement due to residual surface roughness. The fact that the Raman scattering by crystal violet molecules on a "smooth" Au surface is greater than by crystal violet molecules on a Ag surface, which is opposite to what one would expect on the basis of mechanisms that depend on the magnitudes of the real and imaginary parts of the dielectric constant of the metal substrate, provides clearcut evidence for contributions that depend on the specific nature of the chemisorption of the molecules by the metal substrate.

### III LIST OF PARTICIPATING PERSONNEL

A. Brotman	Graduate Student, supported by ARO May 1 to October 31, 1981, doing research on Raman scattering by molecules at metal surfaces.
E. Burstein	Principal Investigator
L.Y. Ching	Graduate Student supported full time by ARO, October 1, 1979 to September 30, 1980, received PhD May, 1980 on "Resonant Raman Scattering at InAs Surfaces and Interfaces".
H. Levinson	Research Investigator supported half time by ARO, September 1, 1980 to January 31, 1981 doing research on optical phenomena at metal surfaces in ultrahigh vacuum.
G. Ritchie	Graduate Student supported by ARO, January 1 to May 30, 1981, doing research on Raman scattering by adsorbed molecules at metal surfaces.
H. Talaat	Research Investigator supported in part by ARO, June 1 to October 31, 1981 doing research on Raman scattering by adsorbed molecules at metal surfaces.

#### IV. LIST OF PUBLICATIONS

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